New Approach to Durability of Glassceramic and Silicate Glass

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Abstract

The goal of this work is to determine correlation of amorphous nonmetallic materials with defective surface layers and their physical properties. Microcreep processes in tested materials can be described by general equation that is known as logarithmic microcreep equation. Applicability of this equation for tested optical materials is indicative for microcreep processes in crystalline and amorphous hard materials. For each grade of polished optical glass, minimal residual defective layer exists. Parameters of this layer are interrelated with mechanical properties of glassceramics and glass, such as microhardness and optical strain coefficient, and thermophysical properties, such as thermal diffusivity, sintering temperature, and annealing temperature. It is first suggested to estimate durability of optical silicate glass and glassceramic, using $E \cdot a^{1/2}$ parameter (E -elasticity modulus, a - thermal diffusivity).

Keywords

Defective Layer; Microcreep; Durability; Glassceramic; Glass

Introduction

The structure and behavior of surface layers of crystals under external mechanical actions were analyzed by Alekhin in [1]. Using silicon and germanium single crystals as test samples, he found the common regularity of the surface microplasticity, which consists in the fact that at the initial loading stages the gradient distribution of dislocations within the near-surface sample layers, up to several tens of micrometers in thickness, takes place. The study using a low-energy electron diffraction [2, 3] showed that atoms of crystal surface layers were essentially displaced relative to their normal positions in the crystal lattice due to the asymmetry of interatomic forces. Therefore, complex two-dimensional structures having other lattice symmetry, density, length and type of interatomic bonds are formed in the crystal surface layers. The special features of the lattice dynamics and the variations of the lattice

thermodynamic functions are responsible for the higher deformation ability of the crystal surface layers and increased velocity of dislocation movement. Crystal surface layers are characterized by the decreased Pierls-Nabarro barriers and a higher activation volume. The surface vacancies contribute to the decrease of the Pierls-Nabarro barriers, making much easier the dislocation movement. Brittle cracks in crystalline materials initiate due to the non-uniformity of the microdeformation in the near-surface layers.

The above studies were not performed for amorphous nonmetallic hard materials. The purpose of this work was using silicate optical glass as an example, to relate the strength of brittle amorphous nonmetallic materials to the parameters of their surface layers and the material physical properties.

Results

The analysis of the effect of the surface state on the microcreep of optical glassceramics, fused quartz, and certain silicate glass like K8, BK10, TK14, and LK6 has shown that even at room temperature the microcreep is recorded. The studies were carried out on a high-sensitive device for the registration of a relative elongation (ε) of the samples measuring 50 x 5 x 0.6 mm. The relative elongation was calculated by the Chebyshev formula [4]

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{8}{3}\left(\frac{\lambda_0 - \lambda_1}{l_0^2}\right), \qquad (1)$$

where λ_0 is the deflection of a foil indicator applied to the sample before loading, λ_1 is the deflection of the indicator after the loading.

The maximal microcreep rate was exhibited by the samples ground with abrasive material M28. The minimal microcreep rate and the residual strain were observed for the samples with distorted surface layers

removed by mechanical polishing or chemical etching by a hydrofluoric acid solution. The kinetics of the microcreep of the studied materials may be found using the following general equation:

$$\varepsilon = \frac{\Delta l}{l_0} = \alpha \cdot \ln \tau + \beta, \qquad (2)$$

The coefficients α and β for the studied optical materials are given in Table 1.

TABLE 1 THE COEFFICIENTS A AND B FOR THE STUDIED OPTICAL MATERIALS

Material	Treatment	$\alpha, 10^6$	$\beta, 10^5$
Quartz glass	Chemical etching in hydrofluoric acid solution	3.6	-1.0
	Mechanical polishing	5.5	-0.6
	Grinding with abrasive material M10	6.7	0.4
	Grinding with abrasive material M28	7.5	1.4
Optical glassceramics CO115M	Chemical etching in hydrofluoric acid solution	3.8	-0.3
	Mechanical polishing	4.8	0.5
	Grinding with abrasive material M10	6.5	1.0
	Grinding with abrasive material M28	8.7	1.8
Silicate glass as K8, BK10, TK14, and LK6	Chemical etching in hydrofluoric acid solution	3.5	-0.2
	Mechanical polishing	3.0	0.3
	Grinding with abrasive material M10	10.0	0.5
	Grinding with abrasive material M28	12.0	1.1

Note:

1. Average grain sizes of M10 and M28 abrasive materials are 10 and 28 μm, respectively.

2. CO115M (Russian analogue of Zerodur - glassceramics with coefficient of thermal expansion equal zero) is thermoresistant nano-filled glass-ceramics.

Equation (2) is known as the equation that describes logarithmic microcreep of metals and alloys. The applicability of this equation to tested optical materials indicates that microcreep processes are common to crystalline and noncrystalline hard materials. The possibility of the existence of structural microdiscontinuities like dislocations in noncrystalline materials is discussed in [5, 6].

The experimental results obtained in tension studies [4] give grounds to suggest that there is a set of local sources of displacement of interatomic bonds in the studied materials. The concentration of the local sources depends on the preceding machining of the material surface. Under the action of external mechanical stresses, these sources are gradually included in the common microdeformation process until the saturation state is achieved. For this reason, the saturation state in material samples with a thick distorted layer is achieved at the large values of relative elongation. The presence of the distorted surface layer increases the amount of near-surface defects, which are displaced under the action of the constant external load and thermal fluctuations, reducing the elasticity of the surface layer.

The removal of the distorted layer reduces the relative elongation of the sample approximately by a factor of 2, when using mechanical polishing, and by a factor of 1.5 − 6, when using chemical etching in hydrofluoric acid solution, as compared to the initial ground samples.

It has been established that the product of the strength (σ) by the relative elongation (ε) of a sample at creeping is constant for a specified temperature and material [7, 8]. The physical meaning of this parameter is defined as the external force work on microdeformation that is required for the destruction of a unit volume of the material. If this work is constant for each material and does not depend on the condition of the material surface, the strength of the material sample after grinding (σ_g) may be determined by the strength of the polished material sample (σ_0):

$$\sigma_g = \sigma_0 \frac{\varepsilon_0}{\varepsilon_g}. \qquad (3)$$

where ε_0 is the relative elongation of the polished sample, and ε_g is the relative elongation of the ground sample at steady creeping.

Of theoretical and practical interest is to consider the interrelation between the parameters of the polished surface condition of the optical glass sample and the physical properties of the glass.

For the analysis, samples of optical glasses of commercial grades were used, such as flint glass TF10, TF7, TF1, and BF28 and crown glass BK10, STK3, TK23, K8, and LK7. The physical properties of these

materials are given in GOST 13659-78 "Optical colorless glass - Physical and chemical properties - Basic parameters" (USSR State Standard).

Previously it was proposed [9-13] to use ellipsometric parameters of substances, specifically the minimal ellipticity, to describe the parameters characterizing the condition of the distorted surface layer of crystalline, amorphous, or glassceramics. The ellipsometric parameters are ellipticity (tgρ) and phase difference (Δ) between the *p* and *s* components of the electric field vector of the optical wave reflected from the glass sample surface. The values of these parameters are defined by the light and material interaction.

For isotropic dielectrics, the intensity of the *p* component of the electric field vector at a Brewster angle (φ_B) and the ellipticity (tgρ) are zero, and the phase difference (Δ) changes from π (if $\varphi < \varphi_B$) to 0 (if $\varphi > \varphi_B$).

The reason for the use of this method is the fact that the mechanical grinding and polishing of the surface bring about the initiation of brittle cracks and deformation of interatomic bonds in the material, thus reducing the refraction coefficient and change the minimal ellipticity of the material. All the surface layers with microcracks (a relief layer, a fractured layer, and a layer with deformed structure) are characterized by deformed and dangling interatomic bonds. The distribution of defects in the distorted layer may be analyzed by layer-by-layer removing each distorted layer by polishing and measuring the minimal ellipticity at each stage of the removal.

A typical experimental relation of the change of the ellipticity in layer-by-layer removal of distorted layers by polishing may be written by Eq. (4)

$$\text{tg}\rho = (\text{tg}\rho_0 - \text{tg}\rho_{\min})e^{-bx}, \qquad (4)$$

where $tg\rho_0$ is the ellipticity of the polished surface with maximal distortions, $tg\rho_{min}$ is the minimal ellipticity after removing all distorted layers by polishing, *b* is constant for the given material, and *x* is the distance from the treated surface.

The found dependence of the distribution of defects in a distorted layer and a comparison of our data with the results [14] allow us to represent the material machining as a continuous process of the defect accumulation in the near-surface layer, which results in the separation of worn out particles from the surface machined.

The interaction of abrasive grains with the glass surface in machining can be presented as a combination of the indentation of abrasive grains into the material, scratching of the material surface, and initiation of brittle microcracks. According to [15], the propagation of a brittle microcrack in a glass is accompanied with the generation of thermal energy at a distance of several tens of Angstrom unit from the tip of a microcrack. As a result, the temperature within this area increases up to the glass sintering temperature (several hundred degrees C). So, the formation of the distorted layer is accompanied with the temperature changes induced by nonstationary local thermal processes that coincide with the thermal diffusivity of the workpiece material in physical meaning.

Of interest is to relate the experimental values of the distorted layer parameter $tg\rho$ to the thermal diffusivity of the workpiece material. For this purpose, a physical model was proposed, according to which the distribution of distortions in the surface layer is identical to the distribution of thermal energy needed to transfer it into the bulk of the material [16]. For this reason, the thermal diffusivity of the material can be used as a parameter characterizing the process of the material machining.

The experimental data show that, for each glass grade, the minimal residual ellipticity ($tg\rho_{min}$) remains even after thorough (deep) polishing of the glass surface. A comparison of $tg\rho_{min}$ for each glass grade with the glass physical properties has made it possible to determine the dependence of this parameter on the mechanical properties of glass, like microhardness (H) and optical strain coefficient (B), and on thermophysical properties, such as thermal diffusivity (a), sintering temperature (T_s), and annealing temperature (T_a). The greater are the values of these properties, the less is the value of the parameter $tg\rho_{min}$ (see Fig.1–3).
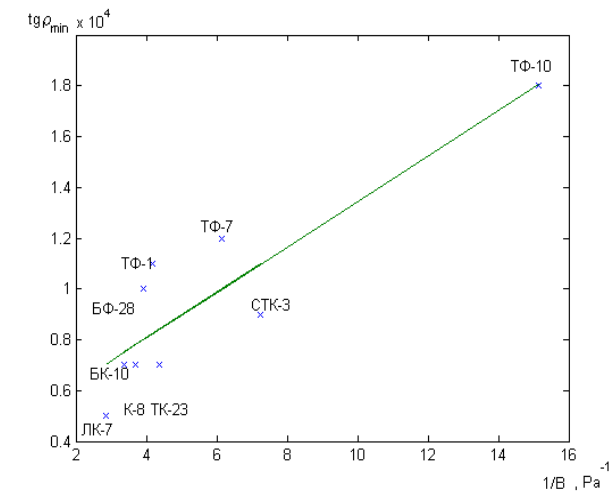
As can be seen from Fig. 1–3, the mechanical and thermophysical properties of the studied material affect the formation and parameters of the distorted surface layer. It may be suggested that the polished surface layer is an analog of the zone with deformation of interatomic bonds at the tip of a crack in the material (see Fig. 4).
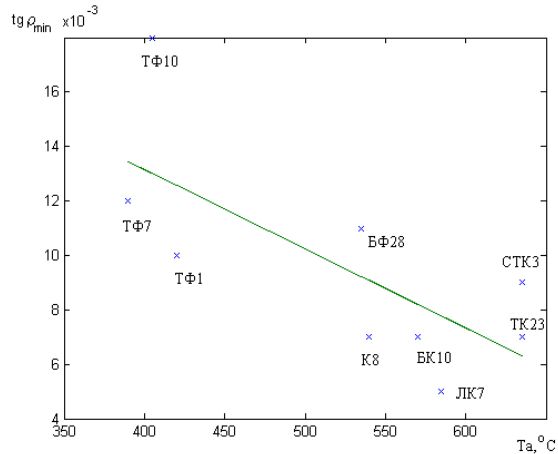
(a)
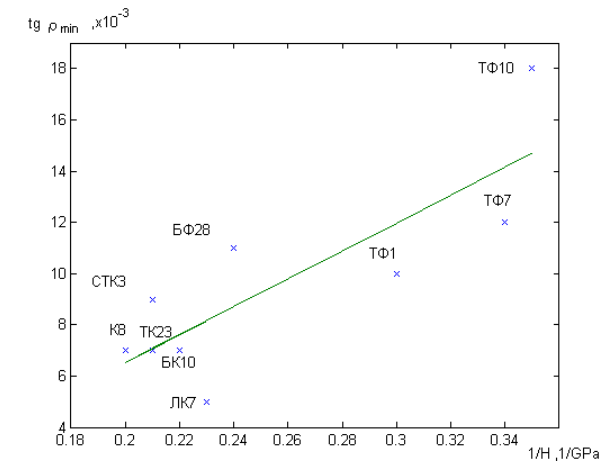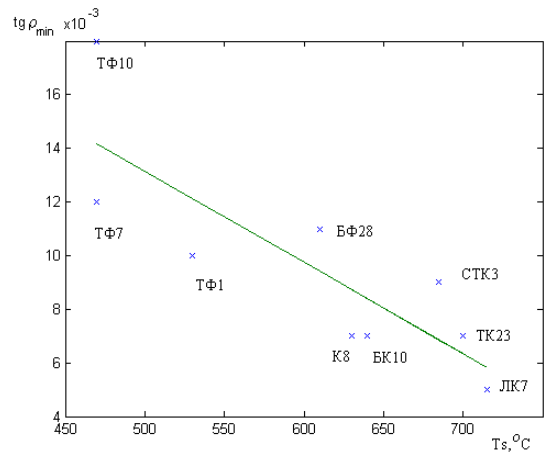
(b)

FIG. 1 MINIMAL ELLIPTICITY FOR A POLISHED SURFACE OF OPTICAL GLASS VS. MICROHARDNESS (A) AND THE OPTICAL STRAIN COEFFICIENT (B)

(a)

(b)

FIG. 3 MINIMAL ELLIPTICITY FOR A POLISHED SURFACE OF OPTICAL GLASS VS. SINTERING (A), AND ANNEALING (B) TEMPERATURE OF THE GLASS
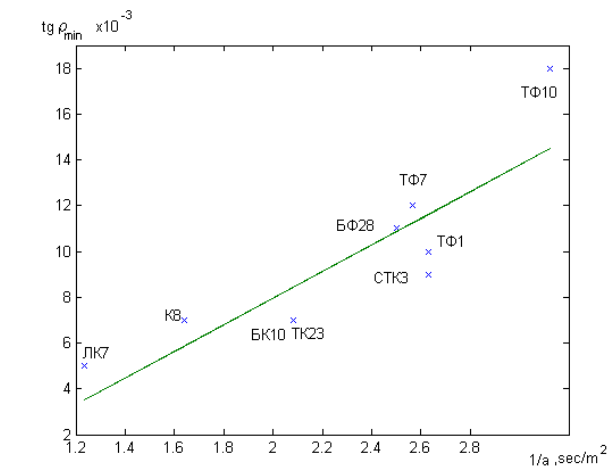

FIG. 2 MINIMAL ELLIPTICITY FOR A POLISHED SURFACE OF OPTICAL GLASS AS A FUNCTION THE THERMAL DIFFUSIVITY OF THE GLASS
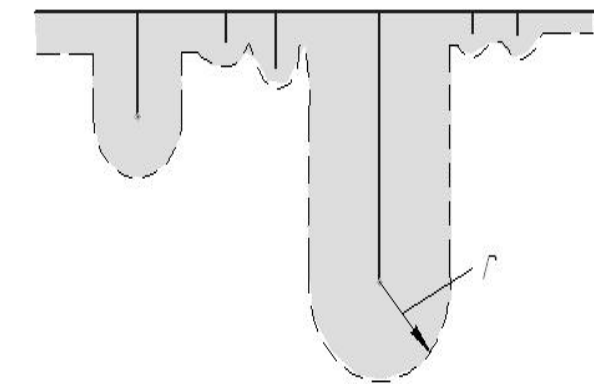

FIG. 4 SCHEMATIC OF THE DISTORTED SURFACE LAYER STRUCTURE WITH MICROCRACKS AFTER MECHANICAL POLISHING (R IS THE RADIUS OF THE DEFORMATION ZONE WITH DANGLING INTERATOMIC BONDS AT THE TIP OF A CRACK)

Fig. 5 illustrates the microstructure of the polished surface of the Zerodur glass ceramics after chemical etching, which supports the schematic shown in Fig. 4.
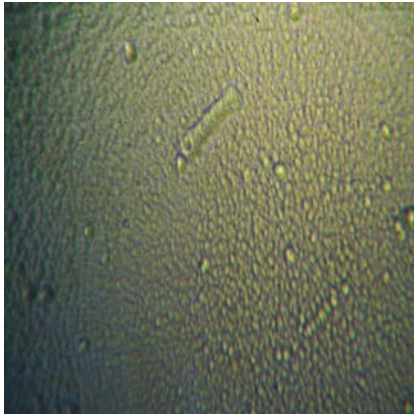

FIG. 5 MICROSTRUCTURE OF THE POLISHED SURFACE OF THE ZERODUR GLASSCERAMICS SAMPLE AFTER CHEMICAL ETCHING (X600)

Discussion

The radius (r) of the deformation zone with dangling interatomic bonds at the tip of a crack can be expressed in terms of the parameter tg$_{Qmin}$:

$$r = k \cdot tg_{Qmin} = k \cdot 1/a, \tag{5}$$

where k is the coefficient of proportionality, a = 1/tg $_{Qmin}$ is the thermal diffusivity of the material.

According to Griffiths [17] and Inglis 18], the strength of brittle materials can be determined as follows:

$$\sigma = (8E\gamma/\pi r)^{1/2}, \tag{6}$$

where E is the elasticity modulus, γ is the specific surface energy.

Taking into consideration (5) and the fact that the specific surface energy is proportional to the elasticity modulus, equation (6) can be expressed as follows:

$$\sigma = A \cdot E \cdot a^{1/2}, \tag{7}$$

where A is the coefficient of proportionality.

The values of the thermal diffusivity of the material can be found in reference book or calculated by the following equation:

$$a = \lambda/C_P d, \tag{8}$$

where λ is the thermal conductivity, C_P is the specific heat capacity, and d is the density of the material.

Fig. 6 shows the durability values for 23 grades of optical glass as a function of the parameter $E \cdot a^{1/2}$. The durability values were taken from [19], and the elasticity modulus values were taken from GOST 13659-78.
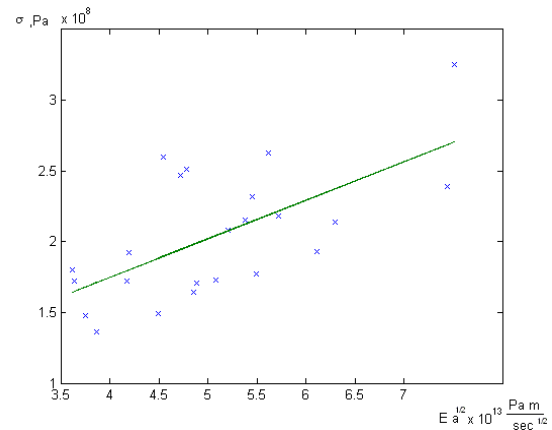

FIG. 6 DURABILITY VALUES OF SILICATE GLASSES AS A FUNCTION OF THE E·A$^{1/2}$ PARAMETER.

The coefficient of proportionality A can be determined from Fig. 6 as follows:

$$\sigma_x = 4 \, (E \, a^{1/2})_x, \text{Мпа}, \tag{9}$$

where index x designates the corresponding to unknown glass.

The use of Eq. (9) provides a possibility to determine the strength of most known of silicate glass with an error of no more than 30 %.

Conclusions

The microcreep processes in glass or glassceramics can be described by a general equation that is known as the logarithmic microcreep equation. The applicability of this equation for studied optical materials is indicative for microcreep processes in crystalline and amorphous hard materials.

A minimal residual distorted layer exists for polished optical glass and glassceramics. These layer parameters depend on mechanical (microhardness and optical strain coefficient) and thermophysical (thermal diffusivity, sintering and annealing temperature) properties of glass.

It is first suggested to estimate durability of optical silicate glass and glassceramic, using $E \, a^{1/2}$ parameter (E -elasticity modulus, a - thermal diffusivity)

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